

# The Sonogashira Reaction on Quinolizinium Cations

Domingo García, Ana M. Cuadro,\* Julio Alvarez-Builla,  
and Juan J. Vaquero\*

*Departamento de Química Orgánica, Universidad de Alcalá*  
28871-Alcalá de Henares, Madrid. Spain  
*juanjose.vaquero@uah.es*

## Supporting Information

Experimental procedures and characterization data  
for all new compounds reported  
(8 pages )

## Experimental section

**General.** Melting points were uncorrected. Infrared spectra were recorded on KBr or NaCl pellets and spectral bands were reported in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded at 200 and 300 MHz and  $^{13}\text{C}$  NMR at 50 and 75 MHz. Chemical shifts were reported as  $\delta$  values (ppm). Low-resolution mass spectra (MS) were obtained as ESI (Na). CuI,  $\text{PdCl}_2(\text{PPh}_3)_2$ , were purchased from Aldrich. The acetylenes: triisopropylsilylacetylene, trimethylsilylacetylene, 1-ethynyl-4-methyl-benzene, 1-ethynyl-4-methoxy-benzene, 1-ethynyl-4-trifluoromethyl-benzene and 2-ethynylpyridine were purchased from Aldrich and were used without further purification. 1-Bromo-3-ethynylbenzene was obtained by a previously described method.<sup>1</sup> DMF, DMAC and  $\text{Et}_3\text{N}$  were distilled over activated molecular sieves.

### Sonogashira Reactions on Quinolizinium Salts 5a-d. General Procedure for the Synthesis of Substituted Quinolizinium Cations 1-4.

**Method A.** A flame-dried vial was charged under argon with 50 mg (0.173 mmol) of the corresponding bromoquinolizinium salt, 10 mol % CuI (3.3 mg, 0.0173 mmol) and 5 mol %  $\text{PdCl}_2(\text{PPh}_3)_2$  (6.9 mg, 0.0087 mmol) in dry DMF (2.5 mL). Then the corresponding acetylene (0.208 mmol) and  $\text{Et}_3\text{N}$  (0.259 mmol, 45  $\mu\text{L}$ ) were added. After heating at 60 °C for 14 h, the solution was filtered through a small pad of celite and washed with methanol (5 mL). The solution was concentrated, treated with a saturated solution of  $\text{NaHCO}_3$  (20 mL) and extracted with EtOAc (15 mL). The organic phase was extracted with  $\text{H}_2\text{O}$  (2 x 10 mL), the aqueous

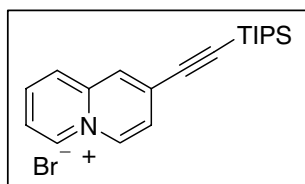
---

<sup>1</sup> Wettergren, J.; Minidis, A. B. E. *Tetrahedron Lett.* **2003**, 16, 4467.

phase was treated with a saturated solution of  $\text{NH}_4\text{PF}_6$  and the resulting phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 15 mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ , the solvent evaporated under reduced pressure and the product isolated by column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (9.6:0.4) as eluent.

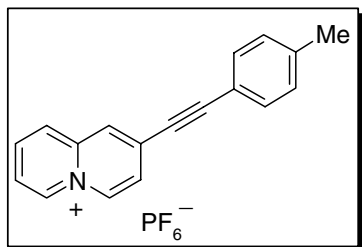
**Method B.** A flame-dried vial was charged under argon with 50 mg (0.173 mmol) of the corresponding bromoquinolizinium salt, 10 mol %  $\text{CuI}$  (3.3 mg, 0.0173 mmol) and 5 mol %  $\text{PdCl}_2(\text{PPh}_3)_2$  (6.9 mg, 0.0087 mmol) in dry DMF (2.5 mL). Then 1.2 equiv. of the corresponding acetylene (0.208 mmol) and 1.5 equiv. of  $\text{Et}_3\text{N}$  (0.259 mmol, 45  $\mu\text{L}$ ) were added. After heating at 60  $^\circ\text{C}$  for 14 h, the solution was filtered through a small pad of celite and washed with methanol (5 mL). The solution was concentrated, treated with  $\text{H}_2\text{O}$  (20 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 15 mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ , the solvent evaporated under reduced pressure and the product isolated by column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (9.6:0.4) as eluent.

#### 2-(Triisopropylsilylethynyl)quinolizinium bromide (2a).



Following the general procedure B, from **5b** and triisopropylsilylacetylene (47  $\mu\text{L}$ ), were obtained 55.6 mg (82%) of **2a** as a yellow solid: mp 206-208  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$ ); IR (NaCl) 2944, 1866, 2154, 1642, 1450, 1402, 1152, 883  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (200 MHz, Acetone- $d_6$ ):  $\delta$  10.22 (d, 1H,  $J$  = 6.4 Hz), 10.19 (d, 1H,  $J$  = 7.2 Hz), 8.22 (s, 1H), 8.72 (d, 1H,  $J$  = 8.5 Hz), 8.51 (ddd, 1H,  $J$  = 8.5, 7.3, 1.0 Hz), 8.18 (ddd, 1H,  $J$  = 8.2, 6.9, 1.3 Hz), 8.09 (dd, 1H,  $J$  = 7.2, 1.8 Hz), 1.21-1.14 (m, 21H);  $^{13}\text{C}$  RMN (50 MHz, Acetone- $d_6$ ):  $\delta$  143.7, 138.6, 138.3, 137.9, 131.4, 130.3, 127.9, 125.8, 124.9, 104.1, 103.3, 18.9, 11.8. MS (ESI $^+$ )  $m/z$  310 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{BrNSi}$ : C, 61.53; H, 7.23; N, 3.59. Found: C, 61.69; H, 7.41; N, 3.60.

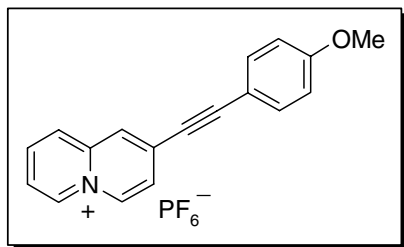
#### 2-(4-Methylphenylethynyl)quinolizinium hexafluorophosphate (2b).



Following the general procedure A, from **5b** and 1-ethynyl-4-methyl-benzene (24.2 mg), were obtained 49.4 mg (74%) of **2b** as a white solid: mp 205-207  $^\circ\text{C}$  ( $\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$ ); IR (KBr) 2209, 1646, 1451, 1407, 1147, 837  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.42 (d, 2H,  $J$  = 7.0 Hz), 8.74 (s,

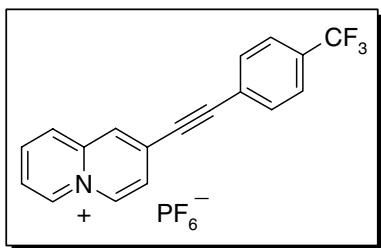
1H), 8.63 (d, 1H,  $J = 8.4$  Hz), 8.51 (t, 1H,  $J = 7.3$  Hz), 8.21-8.19 (m, 2H), 7.59 (d, 2H,  $J = 8.1$  Hz), 7.35 (d, 2H,  $J = 7.9$  Hz), 2.40 (s, 3H);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  143.5, 141.8, 138.3, 137.6, 137.3, 132.7, 132.2, 130.1, 129.1, 127.7, 125.7, 124.7, 118.2, 101.0, 85.7, 21.6. MS (ESI $^+$ )  $m/z$  244 ( $M^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_6\text{NP}$ : C, 55.54; H, 3.63; N, 3.60. Found: C, 55.60; H, 3.67; N, 3.39.

## 2-(4-Methoxyphenylethynyl)quinolizinium hexafluorophosphate (2c).



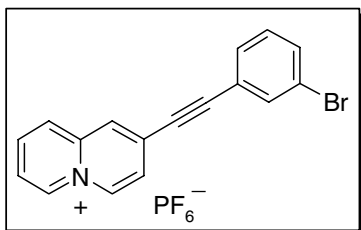
Following the general procedure A, from **5b** and 1-ethynyl-4-methoxy-benzene (27  $\mu\text{l}$ ), were obtained 54.9 mg (78%) of **2c** as a yellow solid: mp 195-196  $^{\circ}\text{C}$  ( $\text{CH}_2\text{Cl}_2\text{:Et}_2\text{O}$ ); IR (KBr) 3118, 2854, 2202, 1647, 1599, 1255, 842  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.37 (d, 2H,  $J = 7.0$  Hz), 8.70 (s, 1H), 8.60 (d, 1H,  $J = 8.4$  Hz), 8.49 (td, 1H,  $J = 7.9, 0.9$  Hz), 8.19-8.15 (m, 2H), 7.66 (d, 2H,  $J = 8.8$  Hz), 7.07 (d, 2H,  $J = 8.9$  Hz), 3.89 (s, 3H);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  162.7, 144.0, 138.6, 138.0, 137.6, 135.1, 133.0, 129.0, 128.0, 126.0, 124.9, 115.5, 113.4, 102.0, 85.8, 55.9. MS (ESI $^+$ )  $m/z$  260 ( $M^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_6\text{NOP}$ : C, 53.35; H, 3.48; N, 3.46. Found: C, 53.46; H, 3.57; N, 3.68.

## 2-(4-Trifluoromethylphenylethynyl)-quinolizinium hexafluorophosphate (2d).



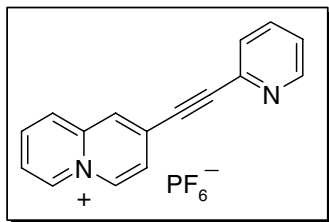
Following the general procedure A, from **5b** and 1-ethynyl-4-trifluoromethyl-benzene (34  $\mu\text{l}$ ), were obtained 52.6 mg (69%) of **2d** as a white solid: mp 213-214  $^{\circ}\text{C}$  ( $\text{CH}_2\text{Cl}_2\text{:Et}_2\text{O}$ ); IR (KBr) 3109, 2226, 1643, 1409, 1327, 1132, 1067, 838  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.44 (d, 2H,  $J = 7.0$  Hz), 8.85 (s, 1H), 8.66 (d, 1H,  $J = 8.6$  Hz), 8.56 (td, 1H,  $J = 7.1, 0.9$  Hz), 8.28-8.22 (m, 2H), 7.94 (d, 2H,  $J = 8.2$  Hz), 7.87 (d, 2H,  $J = 8.2$  Hz);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  144.0, 139.1, 138.4, 137.9, 133.8, 132.2 (c,  $J = 32.3$  Hz), 131.6, 130.5, 128.4, 126.7 (c,  $J = 2.9$  Hz), 126.1, 125.8, 125.6, 124.7 (c,  $J = 253.7$  Hz), 98.3, 88.0. MS (ESI $^+$ )  $m/z$  298 ( $M^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{11}\text{F}_9\text{NP}$ : C, 48.78; H, 2.50; N, 3.16. Found: C, 48.89; H, 2.31; N, 3.25.

### 2-(3-Bromophenylethynyl)quinolizinium hexafluorophosphate (**2e**).



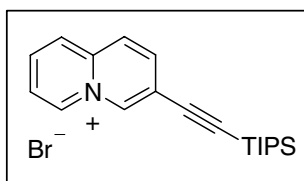
Following the general procedure A, from **5b** and 1-bromo-3-ethynyl-benzene (37.6 mg), were obtained 55.7 mg (71%) of **2e** as a white solid: mp 220-222 °C (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O); IR (KBr) 3111, 2234, 2218, 1643, 1451, 1409, 1151, 844 cm<sup>-1</sup>; <sup>1</sup>H RMN (200 MHz, Acetone-*d*<sub>6</sub>): δ 9.41 (d, 2H, *J* = 7.2 Hz), 8.79 (s, 1H), 8.64 (d, 1H, *J* = 8.2 Hz), 8.53 (td, 1H, *J* = 8.0, 0.8 Hz), 8.25-8.18 (m, 2H), 7.88 (t, 1H, *J* = 1.8 Hz), 7.77-7.69 (m, 2H), 7.48 (t, 1H, *J* = 7.7 Hz); <sup>13</sup>C RMN (50 MHz, Acetone-*d*<sub>6</sub>): δ 143.9, 139.0, 138.2, 137.8, 135.5, 134.5, 132.0, 131.8, 130.2, 128.3, 126.1, 125.4, 123.9, 122.9, 98.5, 87.2. MS (ESI<sup>+</sup>) *m/z* 310 (M<sup>+</sup>+1, 98), 308 (M<sup>+</sup>-1, 100). Anal. Calcd for C<sub>17</sub>H<sub>11</sub>BrF<sub>6</sub>NP: C, 44.96; H, 2.44; N, 3.08. Found: C, 44.80; H, 2.35; N, 3.33.

### 2-(Pyridin-2-ylethynyl)quinolizinium hexafluorophosphate (**2f**).



Following the general procedure A, from **5b** and 2-ethynyl-pyridine (21.4 mg), were obtained 28.2 mg (43%) of **2f** as a white solid: mp 219-222 °C (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O); IR (KBr) 3111, 2213, 1643, 1618, 1449, 1408, 831 cm<sup>-1</sup>; <sup>1</sup>H RMN (300 MHz, Acetone-*d*<sub>6</sub>): δ 9.44 (d, 2H, *J* = 7.1 Hz), 8.86 (s, 1H), 8.72 (d, 1H, *J* = 4.8 Hz), 8.67 (d, 1H, *J* = 8.6 Hz), 8.56 (ddd, 1H, *J* = 8.6, 8.3, 1.1 Hz), 8.28-8.22 (m, 2H), 7.95 (td, 1H, *J* = 7.7, 1.7 Hz), 7.80 (dt, 1H, *J* = 7.7, 1.1 Hz), 7.53 (ddd, 1H, *J* = 7.7, 6.0, 1.1 Hz); <sup>13</sup>C RMN (75 MHz, Acetone-*d*<sub>6</sub>): δ 151.3, 143.7, 141.9, 138.9, 138.1, 137.7, 137.5, 131.3, 130.5, 129.1, 128.1, 125.9, 125.5, 125.4, 98.8, 84.1. MS (ESI<sup>+</sup>) *m/z* 231 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>16</sub>H<sub>11</sub>F<sub>6</sub>N<sub>2</sub>P: C, 51.08; H, 2.95; N, 7.45. Found: C, 51.32; H, 2.71; N, 7.70.

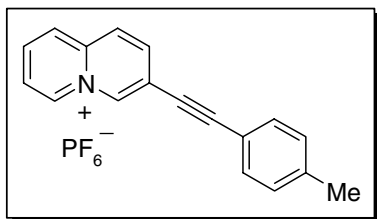
### 3-(Triisopropylsilanylethynyl)quinolizinium hexafluorophosphate (**3a**).



Following the general procedure B, from **5c** and triisopropylsilylacetylene (47 μl), were obtained 54.2 mg (80%) of **3a** as a yellow solid: mp 70-72 °C (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O); IR (NaCl) 2944, 2865, 2163, 1626, 1463, 1398, 1222, 996, 882 cm<sup>-1</sup>; <sup>1</sup>H RMN (300 MHz, Acetone-*d*<sub>6</sub>): δ 10.03 (s, 1H), 9.81 (d, 1H, *J* = 6.6 Hz), 8.76 (t, 2H, *J* = 9.5 Hz), 8.55 (ddd, 1H, *J* = 8.5, 7.3, 1.1 Hz), 8.45 (dd, 1H, *J* = 9.0, 1.7 Hz), 8.26 (t, 1H, *J* = 6.5 Hz), 1.21-1.15 (m, 21H); <sup>13</sup>C RMN (75 MHz, Acetone-*d*<sub>6</sub>): δ 143.0, 140.2, 138.9, 138.6, 137.7,

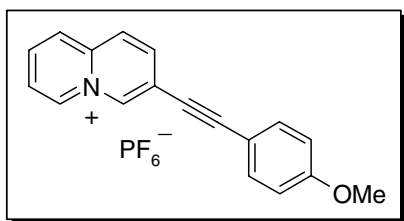
128.2, 128.1, 125.2, 120.2, 100.8, 100.4, 18.9, 11.8. MS (ESI<sup>+</sup>)  $m/z$  310 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>20</sub>H<sub>28</sub>BrNSi: C, 61.53; H, 7.23; N, 3.59. Found: C, 61.42; H, 7.51; N, 3.43.

### 3-*p*-Tolylethynyl-quinolizinium hexafluorophosphate (**3b**).



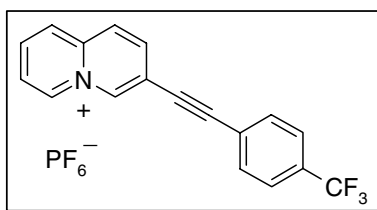
Following the general procedure A, from **5c** and 1-ethynyl-4-methyl-benzene (24.2 mg), were obtained 51.0 mg (76%) of **3b** as a white solid: mp 207-209 °C (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O); IR (KBr) 2924, 2219, 1627, 1517, 1401, 831 cm<sup>-1</sup>; <sup>1</sup>H RMN (200 MHz, Acetone-*d*<sub>6</sub>): δ 9.67 (s, 1H), 9.41 (d, 1H, *J* = 6.7 Hz), 8.71-8.66 (m, 2H), 8.53 (ddd, 2H, *J* = 9.5, 7.9, 1.0 Hz), 8.28 (t, 1H, *J* = 6.9 Hz), 7.55 (d, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 8.0 Hz), 2.40 (s, 3H); <sup>13</sup>C RMN (75 MHz, Acetone-*d*<sub>6</sub>): δ 142.9, 141.6, 139.4, 139.1, 138.6, 137.5, 132.8, 130.4, 128.3, 128.2, 125.8, 121.5, 118.8, 97.9, 83.1, 21.5. MS (ESI<sup>+</sup>)  $m/z$  244 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>F<sub>6</sub>NP: C, 55.54; H, 3.63; N, 3.60. Found: C, 55.25; H, 3.84; N, 3.54.

### 3-(4-Methoxyphenylethynyl)quinolizinium hexafluorophosphate (**3c**).



Following the general procedure A, from **5c** and 1-ethynyl-4-methoxy-benzene (27 μl), were obtained 54.2 mg (77%) of **3c** as a yellow solid: mp 197-198 °C (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O); IR (KBr) 3106, 2853, 2210, 1716, 1629, 1599, 1516, 1254, 842 cm<sup>-1</sup>; <sup>1</sup>H RMN (300 MHz, Acetone-*d*<sub>6</sub>): δ 9.64 (s, 1H), 9.41 (d, 1H, *J* = 6.8 Hz), 8.70 (d, 1H, *J* = 5.3 Hz), 8.67 (d, 1H, *J* = 5.3 Hz), 8.56-8.48 (m, 2H), 8.27 (t, 1H, *J* = 7.0 Hz), 7.61 (d, 2H, *J* = 9.0 Hz), 7.06 (d, 2H, *J* = 9.0 Hz), 3.88 (s, 3H); <sup>13</sup>C RMN (75 MHz, Acetone-*d*<sub>6</sub>): δ 162.2, 142.8, 139.1, 138.4, 137.5, 134.6, 128.3, 128.2, 125.7, 121.9, 115.4, 113.6, 98.2, 94.0, 82.6, 55.9. MS (ESI<sup>+</sup>)  $m/z$  260 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>F<sub>6</sub>NOP: C, 55.35; H, 3.48; N, 3.46. Found: C, 55.12; H, 3.63; N, 3.19.

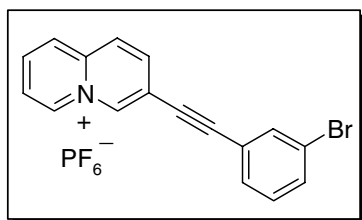
### 3-(4-Trifluoromethylphenylethynyl)quinolizinium hexafluorophosphate (**3d**).



Following the general procedure A, from **5c** and 1-ethynyl-4-trifluoromethyl-benzene (34 μl), were obtained 44.6 mg (58%) of **3d** as a white solid: mp 202-204 °C (CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O); IR (KBr) 3121, 2223, 1629, 1404, 1327,

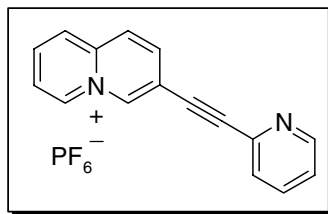
1130, 1067, 839  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.74 (s, 1H), 9.41 (d, 1H,  $J$  = 6.8 Hz), 8.71 (d, 2H,  $J$  = 9.0 Hz), 8.59-8.54 (m, 2H), 8.29 (t, 1H,  $J$  = 7.0 Hz), 7.91 (d, 2H,  $J$  = 8.2 Hz), 7.85 (d, 2H,  $J$  = 8.4 Hz);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  143.3, 140.1, 139.1, 139.0, 137.8, 133.5, 132.8 (c,  $J$  = 32.3 Hz), 128.4, 126.7 (c,  $J$  = 4.4 Hz), 126.0, 125.9, 124.8 (c,  $J$  = 256.6 Hz), 122.9, 120.6, 95.3, 85.6. MS (ESI $^+$ )  $m/z$  298 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{11}\text{F}_9\text{NP}$ : C, 48.78; H, 2.50; N, 3.16. Found: C, 48.53; H, 2.69; N, 3.15.

### 3-(3-Bromophenylethynyl)quinolizinium hexafluorophosphate (3e).



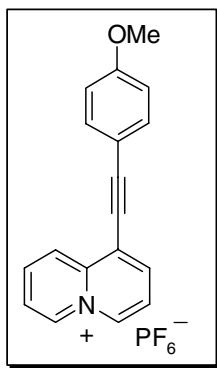
Following the general procedure A, from **5c** and 1-bromo-3-ethynyl-benzene (37.6 mg), were obtained 54.9 mg (70%) of **3e** as a white solid: mp 224-226  $^{\circ}\text{C}$  ( $\text{CH}_2\text{Cl}_2\text{:Et}_2\text{O}$ ); IR (KBr) 3110, 2230, 1627, 1511, 1399, 844  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.71 (s, 1H), 9.41 (d, 1H,  $J$  = 6.8 Hz), 8.71 (d, 2H,  $J$  = 9.0 Hz), 8.56 (td, 2H,  $J$  = 8.4, 1.1 Hz), 8.29 (t, 1H,  $J$  = 6.2 Hz), 7.85 (t, 1H,  $J$  = 1.5 Hz), 7.73 (ddd, 1H,  $J$  = 8.1, 1.8, 0.9 Hz), 7.68 (dt, 1H,  $J$  = 7.9, 1.3 Hz), 7.48 (t, 1H,  $J$  = 8.1, Hz);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  143.0, 139.7, 138.8, 138.7, 137.5, 135.0, 133.9, 131.5, 131.4, 128.1, 125.7, 123.8, 122.7, 120.5, 95.1, 84.6. MS (ESI $^+$ )  $m/z$  310 ( $\text{M}^+ + 1$ , 99), 308 ( $\text{M}^+ - 1$ , 100). Anal. Calcd for  $\text{C}_{17}\text{H}_{11}\text{BrF}_6\text{NP}$ : C, 44.96; H, 2.44; N, 3.08. Found: C, 44.72; H, 2.73; N, 3.03.

### 3-(Pyridin-2-ylethynyl)quinolizinium hexafluorophosphate (3f).



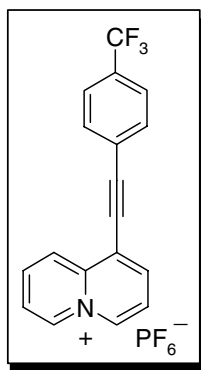
Following the general procedure A, from **5c** and 2-ethynyl-pyridine (21.4 mg), were obtained 32.7 mg (50%) of **3f** as a light brown solid: mp 220-222  $^{\circ}\text{C}$  (Acetone: $\text{Et}_2\text{O}$ ); IR (KBr) 2925, 1628, 1431, 1386, 1841  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.77 (s, 1H), 9.45 (d, 1H,  $J$  = 6.8 Hz), 8.74-8.72 (m, 3H), 8.61-8.55 (m, 2H), 8.31 (t, 1H,  $J$  = 7.1 Hz), 7.94 (td, 1H,  $J$  = 7.8, 1.7 Hz), 7.76 (dt, 1H,  $J$  = 7.9, 0.9 Hz), 7.52 (ddd, 1H,  $J$  = 7.7, 6.0, 1.3 Hz);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  151.3, 143.2, 142.1, 140.3, 139.0, 138.9, 137.7, 137.5, 128.9, 128.3, 125.8, 125.3, 120.4, 96.1, 81.9. MS (ESI $^+$ )  $m/z$  231 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{16}\text{H}_{11}\text{F}_6\text{N}_2\text{P}$ : C, 51.08; H, 2.95; N, 7.45. Found: C, 49.92; H, 3.09; N, 7.36.

#### 1-(4-Methoxy-phenylethynyl)-quinolizinium hexafluorophosphate (**1a**).



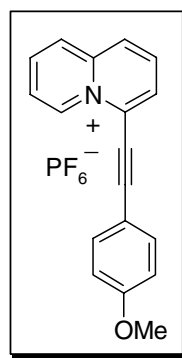
Following the general procedure A, from **5a** and 1-ethynyl-4-methoxybenzene (27  $\mu$ l), were obtained 33.1 mg (47%) of **1a** as a yellow solid: mp 235-237  $^{\circ}$ C; IR (KBr) 3123, 2205, 1638, 1606, 1257, 837, 557  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.51 (d, 1H,  $J$  = 6.8 Hz), 9.39 (d, 1H,  $J$  = 7.0 Hz), 9.11 (d, 1H,  $J$  = 8.6 Hz), 8.66-8.61 (m, 2H), 8.29 (td, 1H,  $J$  = 6.8, 1.3 Hz), 8.21 (t, 1H,  $J$  = 7.2 Hz), 7.74 (d, 2H,  $J$  = 9.0 Hz), 7.08 (d, 2H,  $J$  = 9.0 Hz), 3.89 (s, 3H);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  162.4, 144.2, 139.9, 139.6, 138.9, 137.0, 134.8, 126.8, 125.7, 124.5, 123.1, 115.5, 113.6, 102.2, 81.6, 55.9. MS (ESI $^{+}$ )  $m/z$  260 ( $\text{M}^{+}$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_6\text{NOP}$ : C, 53.53; H, 3.48; N, 3.46. Found: C, 53.40; H, 3.56; N, 3.71.

#### 1-(4-Trifluoromethyl-phenylethynyl)-quinolizinium hexafluorophosphate (**1b**).



Following the general procedure A, from **5a** and 1-ethynyl-4-trifluoromethylbenzene (34  $\mu$ l), afforded 30.7 mg (40%) of **1b** as a white solid: mp 197-199  $^{\circ}$ C; IR (KBr) 3121, 2926, 2224, 1636, 1410, 1326, 1133, 834, 558  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  9.57 (d, 1H,  $J$  = 6.8 Hz), 9.49 (d, 1H,  $J$  = 7.0 Hz), 9.18 (d, 1H,  $J$  = 8.6 Hz), 8.76 (d, 1H,  $J$  = 7.5 Hz), 8.68 (td, 1H,  $J$  = 7.5, 1.1 Hz), 8.35 (t, 1H,  $J$  = 6.0 Hz), 8.27 (t, 1H,  $J$  = 7.1 Hz), 8.04 (d, 2H,  $J$  = 8.1 Hz), 7.89 (d, 2H,  $J$  = 8.2 Hz);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  144.0, 140.9, 139.7, 138.8, 137.8, 133.4, 131.7 (c,  $J$  = 32.1 Hz), 126.5, 126.4, (c,  $J$  = 4.4 Hz), 125.8, 125.7, 124.2, 122.8, 121.7, 99.0, 84.4. MS (ESI $^{+}$ )  $m/z$  298 ( $\text{M}^{+}$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{11}\text{F}_9\text{NP}$ : C, 48.78; H, 2.50; N, 3.16. Found: C, 48.84; H, 2.73; N, 3.28.

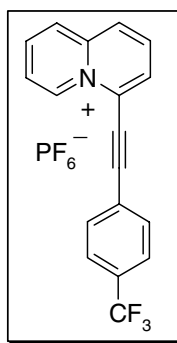
#### 4-(4-Methoxy-phenylethynyl)-quinolizinium hexafluorophosphate (**4a**).



Following the general procedure A, from **5d** and 1-ethynyl-4-methoxybenzene (27  $\mu$ l), stirring at room temperature for 14 h, afforded 43.0 mg (61%) of **4a** as a yellow solid: mp 220-222  $^{\circ}$ C; IR (KBr) 3119, 2201, 1601, 1512, 1258, 839, 558  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  10.08 (d, 1H,  $J$  = 7.0 Hz), 8.77 (d, 1H,  $J$  = 8.4 Hz), 8.70-8.65 (m, 1H), 8.58 (ddd, 1H,  $J$  = 9.7, 7.3, 1.1 Hz), 8.53-8.47 (m, 2H), 8.33 (td, 1H,  $J$  = 7.0, 1.5 Hz), 7.84

(d, 2H,  $J = 9.0$  Hz), 7.13 (d, 2H,  $J = 9.0$  Hz), 3.91 (s, 3H);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  163.2, 144.7, 138.6, 136.9, 135.7, 135.3, 130.4, 129.4, 127.9, 126.0, 119.6, 115.7, 112.3, 107.7, 79.4, 56.1. MS (ESI $^+$ )  $m/z$  260 ( $M^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{F}_6\text{NOP}$ : C, 53.35; H, 3.48; N, 3.46. Found: C, 53.60; H, 3.59; N, 3.27.

**4-(4-Trifluoromethyl-phenylethynyl)-quinolizinium hexafluorophosphate (4b).**



Following the general procedure A, from **5d** and 1-ethynyl-4-trifluoromethyl-benzene (34  $\mu\text{l}$ ), stirring at room temperature for 14 h, afforded 38.4 mg (50%) of **4b** as a white solid: mp 213-215  $^{\circ}\text{C}$ ; IR (KBr) 3121, 2927, 222, 1641, 1618, 1411, 1329, 1129, 1068, 837, 558  $\text{cm}^{-1}$ ;  $^1\text{H}$  RMN (300 MHz, Acetone- $d_6$ ):  $\delta$  10.16 (dd, 1H,  $J = 7.0, 0.9$  Hz), 8.82 (d, 1H,  $J = 8.6$  Hz), 8.77 (d, 1H,  $J = 8.6$  Hz), 8.66-8.61 (m, 2H), 8.54 (t, 1H,  $J = 7.5$  Hz), 8.36 (td, 1H,  $J = 7.1, 1.6$  Hz), 8.13 (d, 2H,  $J = 8.1$  Hz), 7.93 (d, 2H,  $J = 8.1$  Hz);  $^{13}\text{C}$  RMN (75 MHz, Acetone- $d_6$ ):  $\delta$  144.8, 139.1, 136.8, 136.0, 134.0, 132.7 (c,  $J = 32.3$  Hz), 130.6, 129.6, 129.3, 129.1, 126.7 (c,  $J = 3.7$  Hz), 126.3, 124.9, 124.7 (c,  $J = 267.5$  Hz), 104.0, 81.7. MS (ESI $^+$ )  $m/z$  298 ( $M^+$ , 100). Anal. Calcd for  $\text{C}_{18}\text{H}_{11}\text{F}_9\text{NP}$ : C, 48.78; H, 2.50; N, 3.16. Found: C, 48.51; H, 2.66; N, 3.10.